THE CATALYTIC HYDROGENATION OF QUINOLINES

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James Lee Hecht

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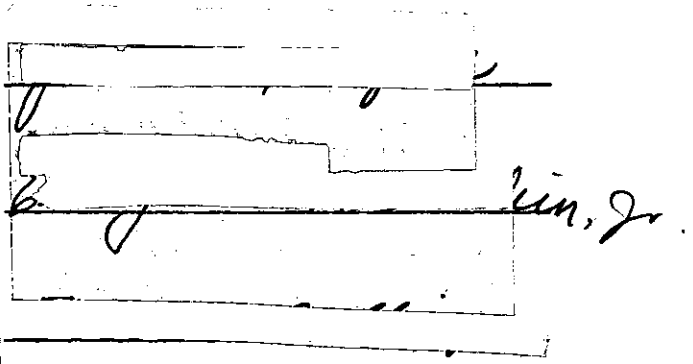

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ABSTRACT

A study was made of the catalytic hydrogenation of quinoline and methyl-substituted quinolines, using an Adams' platinum catalyst with acetic acid as the solvent. A standard Parr Hydrogenation Apparatus was used. The total volume, including the hydrogenation bottle, was 4.43 liters.

The hydrogenation was found to be first order with respect to hydrogen pressure, zero order with respect to concentration of hydrogen acceptor, and zero order with respect to the amount of catalyst used.

Quinoline hydrogenates to 1, 2, 3, 4-tetrahydroquinoline which then hydrogenates to decahydroquinoline. Evidence is presented that some decahydroquinoline is formed before all the quinoline has been hydrogenated to the tetra. The conversion to decahydroquinoline is slowed down by the adsorption of the hydrogenated pyridine nucleus.

The relative rates of the hydrogenation to the tetrahydro form are: quinoline, 1.00; 2-methylquinoline, 0.46; 4-methylquinoline, 0.04; 5-methylquinoline, 0.61; 6-methylquinoline, 0.66; 7-methylquinoline, 0.60; 8-methylquinoline, 1.90. Rate constants for the hydrogenation of the tetrahydro compound to the deca form were also determined.

The energy of activation for the reduction of the pyridine ring is 5,800 calories per mole; for the hydrogenation of the benzene ring it is about 10,000 calories per mole.

With 2-methylquinoline and 4-methylquinoline the rate of reaction decreased rapidly as the hydrogenation proceeded. The available evidence indicates that desorption of one of the tetrahydro derivatives is slow.

THE CATALYTIC HYDROGENATION OF QUINOLINES

I. INTRODUCTION

Because of its importance in both laboratory and industrial syntheses catalytic hydrogenation has been the subject of many thousands of papers. Yet, in spite of these many studies, there is still much doubt about the mechanism of these reactions. Moreover, a satisfactory theory for correlating reactivity with structure has never been suggested.

In 1945 H. A. Smith published the first three of a series of papers which will probably be of great importance in the eventual formation of a satisfactory theory for catalytic hydrogenation (49, 53, 54). He utilized kinetic studies to attack the problem of determining the mechanism of the hydrogenation of an aromatic ring. The initial studies were concerned with the rates of hydrogenation of phenyl-substituted aliphatic acids, benzene and monoalkylbenzenes, and the polymethylbenzenes. These were followed by studies on the hydrogenation of methyl-substituted benzoic acids (55), the cyclohexadienes and cyclohexene (52), the substituted furans (51), and compounds containing two benzene rings (50). In all of these studies rate constants were obtained using an Adams' platinum catalyst (1) with glacial acetic acid as the solvent. Suitable corrections were made for variations in temperature and catalyst, thereby making the rate constants comparable. Their data can be

summarized as follows:

1. The rate is independent of the concentration of hydrogen acceptor;

2. The rate is directly proportional to the amount of catalyst used;

3. The rate is first order with respect to hydrogen pressure;

4. Substitution tends to decrease the reaction rate. When identically substituted compounds are hydrogenated, the symmetrically substituted ones react faster than the others.

In an investigation which has not yet been published, Smith and Stanfield studied the hydrogenation of the pyridine nucleus (56). They noted that the reaction rate decreased with increasing pyridine concentration. It was also observed that as the pressure was decreased the rate of hydrogenation increased. The energy of activation was not constant from 15 °C. to 45 °C. Finally, it was observed that the position of a methyl substituent relative to the nitrogen atom affected the reaction rate. Alpha greater than beta greater than gamma was the order of ease of hydrogenation.

This thesis is a continuation of work started by Stanfield and Trimble in this Laboratory on the hydrogenation of the quinoline nucleus (58). Trimble found that with quinoline the rate of hydrogenation is zero order with respect to the concentration of hydrogen acceptor between concentrations of 0.01 to 0.06 mole per 50 milliliters of acetic acid. He also showed that the rate is directly

proportional to the amount of catalyst.

The purpose of this research is to make a detailed study of the hydrogenation of quinoline and then to observe the effect of substitution on the rate of hydrogenation. The study of the hydrogenation of the quinoline nucleus represents a bold step over previous work, since it involves a double ring system of two different rings. The complications that this induces - such as competitive hydrogenations and a variety of hydrogenation products - are well evidenced in this thesis.

II. THEORETICAL DISCUSSION

A. Factors Influencing the Rate Constant of Liquid-Phase Catalytic Hydrogenations

1. Definition of the Rate Constant:

The rate of hydrogenation of aromatic nuclei, as previously mentioned, has been found to be directly proportional to the hydrogen pressure and the amount of catalyst, and is independent of the concentration of hydrogen-acceptor. Since the amount of catalyst does not change with time, we can say that for a given amount of catalyst

$$\log P_o/P = kt \qquad (1)$$

where P_o is the pressure at the beginning of the run,

P is the pressure at time t, in the same units as P_o,

t is the time, in minutes,

k is the first-order rate constant, in reciprocal minutes.

If the rate constant defined by Equation (1) is divided by the grams of catalyst used, the rate constant then becomes independent of the catalyst concentration. The units of the rate constant are reciprocal minutes per gram.

2. Effect of the Temperature of the Solution:

The change in the rate of hydrogenation with temperature follows approximately the classical Arrhenius Equation:

$$\frac{d \ln k}{dT} = \frac{Ea}{RT^2} \qquad (2)$$

where k is the rate constant, in reciprocal minutes per gram,

T is the absolute temperature, in °K,

R is the gas constant and equals 1.987 calories per gram-mole per °K,

Ea is the apparent energy of activation, in calories per gram-mole.

It should be pointed out that the apparent energy of activation can be quite different from the true energy of activation. A detailed discussion of the significance of the apparent energy of activation can be found in the literature (30).

One of the more useful integrated forms of the Arrhenius Equation is:

$$\ln k = \frac{-Ea}{RT} + \ln pz \qquad (3)$$

where pz is the product of the probability and frequency factors.

Both pz and the apparent energy of activation are capable of physical interpretation. In addition, Equation (3) is useful since it allows comparisons between rate constants taken at different temperatures.

3. Effect of the Volume of the Gas:

Smith and Fuzek (25) have shown that the rate constant is inversely proportional to the volume of the vapor phase. This results because pressures, rather than concentrations, are used. Rate constants obtained with different gaseous volumes can be

easily compared, however, by multiplying the observed constant by the volume.

4. Effect of the Temperature of the Gas:

Although it is not mentioned in the literature, it also follows that the observed rate constant is dependent upon the temperature of the hydrogen gas in the tank.

Consider two hydrogenations, identical in every respect except that the temperatures of the gas, T_1 and T_2 respectively, are different. Then, during a time interval dt, during which dn molecules of hydrogen react in a solution of temperature T_s,

$$dn_1 = dn_2 \tag{4}$$

Since, by the ideal gas law

$$pv = nRT \tag{5}$$

we can say,

$$\left(\frac{dP_1}{dP_2}\right)_{T_s} = \left(\frac{dn_1}{dn_2}\right)\left(\frac{T_1}{T_2}\right)\left(\frac{V_2}{V_1}\right) \tag{6}$$

or, since the volumes are also constant,

$$\left(\frac{dP_1}{dP_2}\right)_{T_s} = \frac{T_1}{T_2} \tag{7}$$

Remembering that

$$dp/dt = kp \tag{8}$$

we see that the observed rate constant is directly proportional to the absolute temperature of the hydrogen gas in the tank.

5. Effect of Solvent:

In any work on catalytic hydrogenation, the nature of the

solvent is of primary importance. Consequently it is not surprising that a number of studies have been directed toward relating solvent with ease of hydrogenation.

Foresti (23) studied the effect of pH on the hydrogenation of benzene and its homologs. He reports that with a platinum catalyst the hydrogenation proceeds much more readily in an acid medium, and that in acid the rate is strongly effected by the pH.

Of considerable interest is the recent work of Baker and Schuetz (5). Using Adams' platinum catalyst at high pressures, they found that hydrogenation of aromatic compounds did not take place when ethanol or dioxane were used as solvents, or when no solvent was used.

The recent work of Withkop (63) is also significant. In his study of the hydrogenation of isoquinoline, using a platinum oxide catalyst in acetic acid, he observed that the addition of a minute amount of sulfuric acid was necessary to hydrogenate the tetrahydro compound to the deca form.

Baker * has recently completed a study on the effect of solvent on the rate of hydrogenation with Adams' platinum catalyst. Using dioxane containing small amounts of acetic acid, he found that the rate was directly dependent upon the concentrations of

* From a paper entitled, "The Mechanism of the Hydrogenation of Benzene". Presented by R. H. Baker at the meeting of the American Chemical Society in Chicago, September, 1950.

the acid and the hydrogen-acceptor. He explains these results on the basis that at low acid concentrations the adsorption of the hydrogen-acceptor is the rate controlling step, the adsorption intermediate being a protonated complex.

To sum up the above results, with a platinum catalyst hydrogenation of an aromatic ring is effective only in acid medium. While this is not true with all other types of catalysts, in all cases the nature of the solvent is an important variable.

6. Effect of the Catalyst:

The rate of the hydrogenation reaction is greatly influenced by the nature of the catalyst. Foremost in importance is the chemical composition. Frequently substances present in extremely small quantities have a very large effect. Likewise, the heat treatment given the catalyst during its preparation is important, since this may determine the lattice structure. The state of division of the catalyst and the mechanical treatment it is subjected to are also important.

Since the rate of reaction is so greatly influenced by catalyst, it is unlikely that two batches of catalyst will have the same activity. However, it is sometimes possible to compare kinetic data taken with different catalysts by using a given reaction as a standard, and then obtaining the relative activities of different catalysts (49).

7. Effect of Agitation:

If the agitation of the hydrogenation bottle is not sufficient, the rate of diffusion of hydrogen to the catalyst surface becomes a rate-controlling step. It has been found, however, that unless the hydrogenation proceeds very rapidly the agitation provided by the Parr apparatus is sufficient to keep the catalyst surface saturated (49).

B. The Catalytic Hydrogenation of Aromatic Rings

The point has already been brought up that our knowledge of the mechanism of the catalytic hydrogenation of aromatic rings is in a very primitive state. As a result, a chapter on this subject can only consist of the hypothesis already advanced, along with a few new ideas, which may help to obtain a clearer picture of the mechanism of catalytic hydrogenation.

1. Review of the Literature.

Our knowledge concerning the mechanism of the catalytic hydrogenation of aromatic rings has greatly increased in the last few years. As a result, most of the theories formulated before 1940 are of interest only from a historical point of view, and will not be considered in this discussion.

The work of Smith and co-workers was mentioned on pages 1 and 2. They have explained their results by considering that the catalyst is covered with a unimolecular layer of hydrogen-acceptor, with the phenyl group absorbed edgewise on the catalyst surface. The rate-controlling step involves the adsorption of hydrogen, and this is sterically hindered by the adsorbed substrate.

Another theoretical contribution by Smith results from studies on the energy of activation. The energy of activation of benzene is 7,400 calories per mole and, since this is much less than the resonance energy, this indicates that such resonance has been destroyed when the benzene is absorbed on the catalyst surface.

Balandin (6, 7) has mathematically treated the kinetics of hydrogenation over a nickel catalyst. He assumes that there are two kinds of active centers; one of these activates hydrogen, while the other activates hydrogen-acceptor. The adsorption equilibria follow the Langmuir isotherm and are more rapid than the subsequent reaction. The hydrogenation itself proceeds through an intermediate half-hydrogenated product.

A somewhat similar view is taken by Herbo (27, 28). His experimental work with a nickel-thoria catalyst led to the conclusion that there are two types of active centers.

Daudel, Pullman, and others have derived a somewhat similar mechanism from quantum mechanical studies (13, 14, 44, 45). Two hydrogen atoms are bonded to mobile electrons on the catalyst surface. A benzene molecule is then bonded at one of its apexes to the surface of the catalyst between the two hydrogen atoms. The adjacent apex takes on a charge and attaches the hydrogen nearest it. This is followed by the remaining hydrogen attaching itself to the other apex. As with Balandin and Herbo, adsorption and desorption are considered to be too rapid to influence the rate. Likewise, hydrogenation is considered to go through an intermediate dihydro compound which is then immediately hydrogenated further.

2. Proposed Theory:

Smith's hypothesis that the rate controlling step may be the adsorption and activation of hydrogen on the catalyst surface is in sharp contrast to the other theories reviewed in the previous section.

While Smith's theory does provide some correlation between structure and reactivity, it is not consistent with a large number of experimental facts.

1. The correlation between structure and reactivity is poor. Benzoic acid hydrogenates only half as rapidly as toluene, but the steric hindrance produced by the two molecules should be about the same. Most convincing is the tremendous difference in the rates of hydrogenation of the quinolines studied in this investigation. 4-methylquinoline hydrogenates only one-fiftieth as rapidly as 8-methylquinoline.

2. Smith assumes a monomolecular layer of hydrogen-acceptor covers the catalyst surface. However, it has been shown by the relative vigorous para-hydrogen conversion which occurs in the presence of benzene that a benzenoid nucleus can not compete with hydrogen for the active centers of the catalyst (20, 21, 31). This would also be expected from a consideration of heats of adsorption. The heat of adsorption for hydrogen is much greater than for benzene (27, 29).

The mechanism postulated by Smith can not explain why cyclohexane retards the hydrogenation of benzene during vapor phase hydrogenation with a nickel catalyst (28). A diminishing of the rate due to the formation of product was also observed in this investigation.

4. As part of the investigation of the hydrogenation of

quinoline it was shown that the adsorption of hydrogen is not the rate-controlling step.

The above irregularities are easily explained if we accept the mechanisms proposed by Balandin, Herbo, Daudel, et al. The variance of reaction rate with structure occurs because of differences in electron densities caused by the changes in structure. The presence of benzene should not effect the rate of the para-hydrogen conversion since it is adsorbed on different active centers. The retardation of the rate of reaction caused by product formation results because product, as well as hydrogen acceptor, is absorbed, thereby cutting down the effective concentration of one of the reactants. Finally, the poisoning effect of free pyridine results because it is adsorbed and held on active centers which would otherwise adsorb and activate hydrogen.

The author, however, would like to suggest one modification. Balandin and Herbo assume there are two different kinds of active centers. Why not consider that the hydrogen-acceptor is adsorbed on a hydrogen atom during the reaction?

Let us consider the advantages of the proposed mechanism, shown in Figure (1) over the mechanism involving two different types of active centers and pictured in Figure 2. We shall consider nickel as our catalyst since it does not involve certain complications which occur with a platinum catalyst.

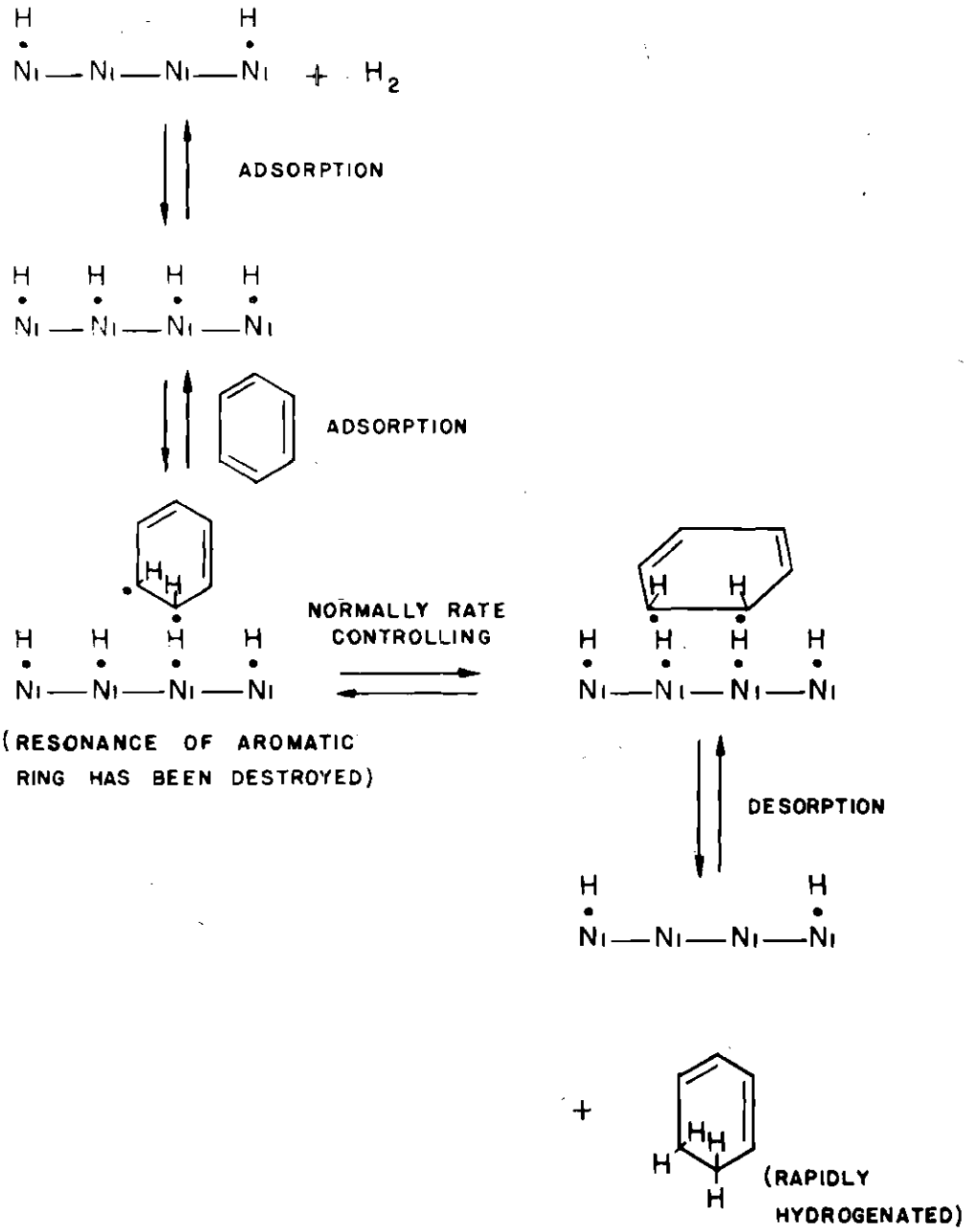

FIGURE 1
PROPOSED MECHANISM OF CATALYTIC HYDROGENATION

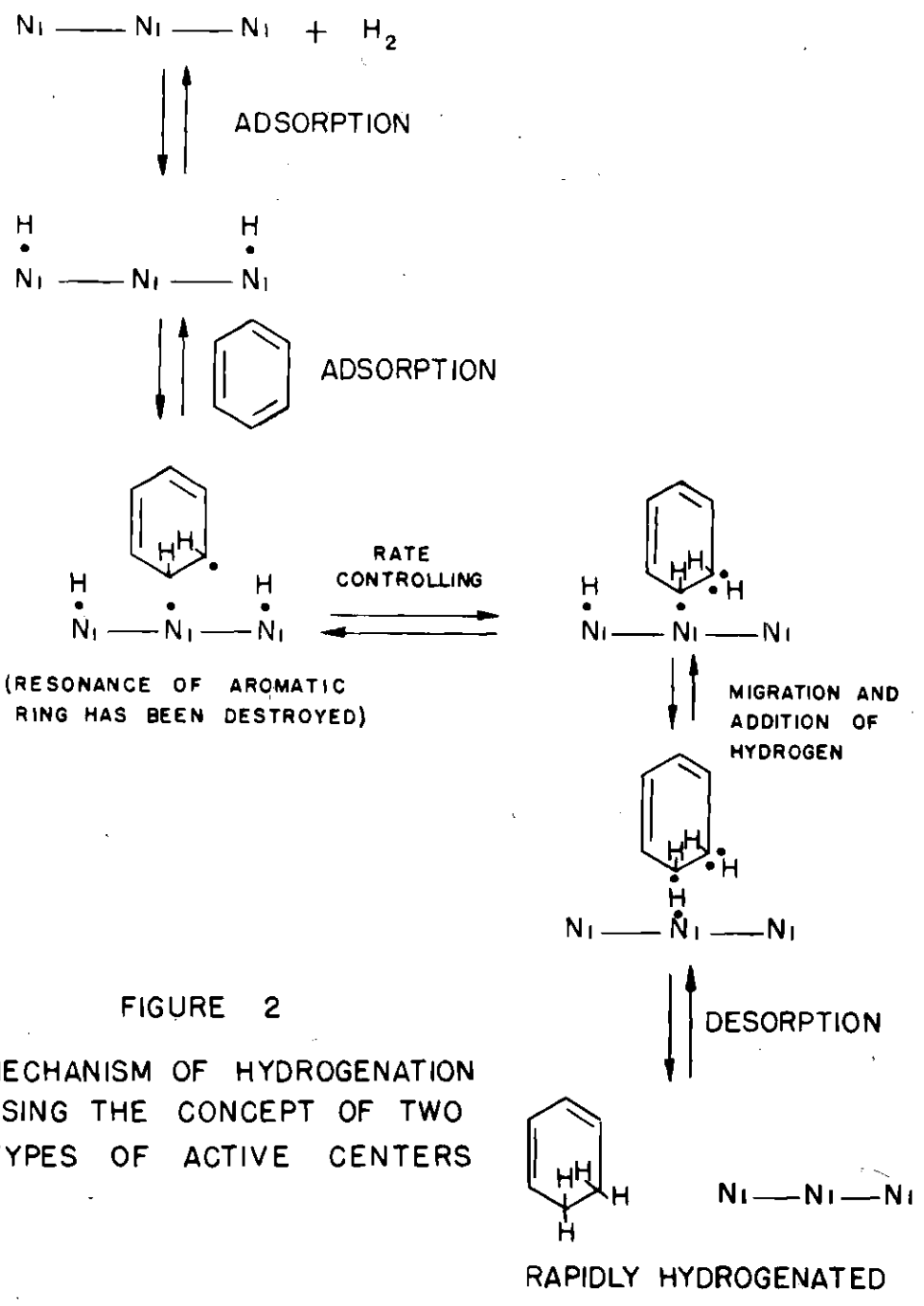

FIGURE 2

MECHANISM OF HYDROGENATION USING THE CONCEPT OF TWO TYPES OF ACTIVE CENTERS

1. The proposed mechanism is certainly reasonable. Adsorption in an outer layer is a generally accepted phenomena. Eley uses the concept of an interaction between a van der Waal's layer and a chemisorbed layer to explain the mechanism of the para-hydrogen conversion (19).

2. The proposed mechanism is more logical from steric considerations. Thus it does not necessitate the migration of a hydrogen atom.

3. Most important, it was observed that if a nickel catalyst is treated with benzene vapor in the absence of hydrogen the activity is reduced to zero (3, 4). Reactivation can be achieved, however, by prolonged treatment with hydrogen. What is happening is that benzene is being adsorbed on active centers that normally would adsorb hydrogen. But, if there are two different types of active centers, this would not be as likely to occur.

4. It is well known that the adsorption of hydrogen and other substances which are chemisorbed results because they contribute free electrons to the electron pool of the catalyst (18). On the other hand, it will be shown in a later section that adsorption of an aromatic ring is favored by an electron deficiency. Obviously the two types of adsorption are fundamentally different. As will be shown later, the proposed mechanism neatly explains this.

In both Figures 1 and 2 the rate-controlling step involves the reaction of adsorbed hydrogen-acceptor with atomic hydrogen. Although it may not be immediately obvious, this does satisfy the kinetic dependence. By the Langmuir isotherm, the concentration of atomic hydrogen, at low pressures, is directly proportional to the pressure

of the gas. The concentration of adsorbed hydrogen-acceptor, on the other hand, does not depend on its concentration as long as there is a sufficient quantity in the solution to keep the area available for adsorption saturated.

Another important item to be stressed in connection with Figures 1 and 2 is that the bond types shown do not necessarily represent the actual bonds. The nature of the bonding in adsorption phenomena is not known. Pollard (43), on the basis of quantum mechanical calculations, considers a one-electron bond the most likely, and this idea has been adopted here.

It is interesting to note that the mechanisms in both Figure 1 and Figure 2 give cis addition exclusively. This agrees with the observation made by Linstead et al (38).

C. Competitive Hydrogenations

A competitive hydrogenation is a hydrogenation in which two or more substances present are capable of being hydrogenated.

Only a few studies have been made on the competitive hydrogenation of aromatic compounds. About the only generalization that can be made is that there is no correlation between the relative rates of compounds hydrogenated singly and in two-component mixtures (16).

A quantitative theory has never been developed for competitive hydrogenations. However, it is simple to develop one from the picture we have drawn of the mechanism of hydrogenation. Let us consider two

substances, 1 and 2, which are to be hydrogenated competitively. It seems reasonable to assume that the ratio of the number of molecules of 1 adsorbed on the catalyst surface to the number of molecules of 2 depends on the molar concentrations in the solution and the tendency towards adsorption. The latter we shall express as the adsorption coefficient fraction. Moreover, it seems probable that the available surface for adsorption will be saturated. Thus we may write at unit pressure

$$n_1 \alpha_1 + n_2 \alpha_2 = S \tag{9}$$

$$\frac{n_1}{n_2} = \frac{a_1 x_1}{a_2 x_2} \tag{10}$$

$$R_H = k_1 n_1 + k_2 n_2 \tag{11}$$

where S is the area available for adsorption,

n is the number of molecules adsorbed,

α is the area covered per adsorbed molecule,

a is the adsorption coefficient,

x is the molar fraction,

k is the absolute rate constant,

R_H is the rate of hydrogenation.

Combining equations 9, 10, and 11

$$R_H = S \left[\frac{k_2 A_2 X_2 + k_1 A_1 X_1}{\alpha_2 A_2 X_2 + \alpha_1 A_1 X_1} \right] \tag{12}$$

and

$$\frac{M_1}{M_2} = \frac{k_1 A_1 X_1}{k_2 A_2 X_2} \tag{13}$$

where M is the moles of hydrogenated product.

Several important points should be stressed in connection with Equations 12 and 13. Most important, the derivation of these equations is based on a concept of hydrogenation which may be wrong. It should also be pointed out that the equations are only exact at the beginning of the hydrogenation, since once product is formed it, too, will be adsorbed. In most cases, however, the adsorption of product will be small for most of the run. Finally, the absolute reaction rate constant should not be thought to be the observed rate. The relation between the two rates can be found by letting either a_2 or x_2 equal zero. Then

$$k_{o_1} = \frac{Sk_1}{\alpha_1} \qquad (14)$$

where k_o is the observed rate.

Equation 12 can be used to derive an equation for the case where we have competitive adsorption. Consider the hydrogenation of a material in the presence of an appreciable amount of product which is adsorbed but can not be hydrogenated further. Then Equation 12 describes the rate of hydrogenation if we allow k_2 to equal zero. If the further simplifying assumption is made that $alpha_1$ equals $alpha_2$, which seems reasonable for structures which sterically are as similar as an aromatic nucleus and its hydrogenated product, then

$$k = \frac{k_o}{1 + Y\left(\frac{x_1}{1 - x_1}\right)} \qquad (15)$$

where Y is a constant equal to a_2/a_1.

k_o is the observed rate constant when x_2 is zero,

k is the observed rate constant,

x is the molar fraction.

D. The Adsorption of Aromatic Molecules

The factors influencing the adsorption of aromatic molecules are important since they determine the magnitude of the absolute adsorption coefficient. These factors are also important since they determine the position at which a molecule is adsorbed.

No one has ever attempted to correlate the readiness of adsorption of an aromatic molecule with structure. From an examination of the available data, however, it appears that adsorption is favored in rings of low electron density. This postulate is based on the following observations.

1. In a previous section it was pointed out that the hydrogenation reaction proceeds best and frequently requires an acid solution. This in itself suggests that a protonated complex, having a low electron density in the ring, is more readily adsorbed than an ordinary aromatic molecule, and this is precisely what Baker has shown in his recent work.

2. In a study of the hydrogenation of pyridines existing as the hydrochlorides, it was found that pyridine was selectively hydrogenated in the presence of 2-picoline, 2-ethylpyridine, 2-propyl-pyridine and 2-phenylpyridine (60). With the possible

exception of the latter, all of the substituted pyridines have electron-feeding groups attached and, since the pyridine ring is positively charged, it seems probable that the phenyl group will also donate electrons to the pyridine ring to a certain extent. On the other hand, with methyl-(2-pyridylmethyl) carbinol or dimethyl-(2-pyridylmethyl) carbinol both the pyridine and the substituted pyridine are hydrogenated. Significantly, with these compounds the substituted groups are not electron donating. It should also be pointed out that with 2-phenyl pyridine the positively charged pyridine ring was hydrogenated in preference to the benzenoid ring.

3. Methyl-substitution, causing an increase in the electron density of the ring, tends to cause hydrogenation to occur in the unsubstituted ring with quinoline and naphthalene (22). This, of course, may also be due to the steric effects in part. However, 2-phenylquinoline hydrogenates completely in the pyridine ring; with 2-methyl quinoline four per cent of the hydrogen enters the benzene ring.

One other adsorption phenomena requires explanation. With a platinum catalyst it appears necessary to have an acidic solution for hydrogenation to occur; with a nickel catalyst it does not. We might consider this due to platinum's greater tendency to hold its electron cloud, as evidenced by its adsorption of hydrogen at low pressures. Thus, considering the electronic diagrams in Figure 1, with nickel an ordinary aromatic nucleus is sufficient to keep the electrons out of the metal. With platinum, however, it is necessary

to have a much lower electron density on the ring in order to prevent the platinum from accumulating the electrons.

EXPERIMENTAL

A. Materials

1. Catalyst:

Two catalysts, both prepared by the American Platinum Company, were used. Catalyst A contained 79.4 per cent platinum, and hydrogenated benzoic acid at a rate of 206 x 10^{-4} reciprocal minutes per gram at 30 °C; catalyst B contained 81.76 per cent platinum and gave a rate constant of 216 x 10^{-4} with benzoic acid.

Spectroscopic analyses of Catalyst B have been made by Mr. P. B. Sherry of this Laboratory. The results are listed in Table I.

2. Acetic Acid:

Glacial acetic acid was purified by distillation through a five-foot column packed with glass helices, containing about 30 theoretical plates. The fraction boiling at 116.6 °C. at 740 mm. pressure was used. This temperature corresponds to a normal boiling point of 118.2 °C; Weissberger (61) gives the normal boiling point of acetic acid as 118.1 °C.

3. Quinolines:

Quinoline, 2-methylquinoline (quinaldine), 4-methylquinoline (lepidine), 6-methylquinoline, 7-methylquinoline, and 8-methylquinoline were obtained from the Eastman Kodak Company and purified by distillation through a six-foot Vigreux column in an atmosphere of nitrogen.

After several unsuccessful attempts to prepare 5-methylquinoline

Table I

Spectroscopic Analysis of Catalyst B

Element	Per Cent Estimated Present
Al	0.0010
Ag	0.0003
As	0.0001
Ca	0.0100
Co	Trace
Cr	0.0001
Cu	0.0001
Fe	0.0010
Hf	Trace
Ir	0.0001
Mg	0.0100
Mn	0.0010
Pb	0.0010
Pd	0.0100
Rb	0.0010
Si	0.0003
Th	Trace
Yb	Trace

by the method of Kulisch (37) *, it was finally prepared as follows. 456 grams of 4-amino,3-nitro-toluene were converted to 4-cyano,3-nitro-toluene by the Sandmeyer reaction (11). The product was recrystallized from a large amount of boiling water to give 75 per cent of the theoretical yield. The product was then reduced to 4-cyano,3-amino-toluene with stannous chloride and hydrochloric acid (8). A 66 per cent yield was obtained. The next step involved a Skraup synthesis (34). 5-methylquinoline-8-carboxylic acid was obtained in 22 per cent yield, along with 6-8 grams of 5-methylquinoline. Unfortunately the decarboxylation of the acid, using the method reported by Seibert and co-workers (48), gave extremely low yields. The trouble may have been that the original investigators failed to report what they meant by a copper-bronze powder. Because of the small quantity of 5-methylquinoline obtained, it was purified by distillation in a small Vigreax column about one foot high. The final product was a colorless liquid with a strong quinoline odor. Upon hydrogenation it adsorbed 104 per cent of the theoretical amount of hydrogen. The four per cent discrepancy is well within the experimental error.

The corrected boiling points of the quinolines used in this work are given in Table II. The distillation temperatures have been corrected for stem exposure to 760 mm. pressure by means of the Clausius-Clapeyron equation and the Kistiakowski equation, the latter being used to estimate the heats of vaporization (17). For purposes

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*See page 51.

Table II

Distillation Temperatures

Compound	Corrected Distillation Temperature, °C	Reported Dist. Temp., °C
Quinoline	238.1	238.1
2-methylquinoline	248.5	247.6
4-methylquinoline	265.0	262
5-methylquinoline	259.9	256
6-methylquinoline	259.1	259
7-methylquinoline	254.0	252
8-methylquinoline	248.5	248.5

of comparison, boiling points listed in Heilbron (26) were corrected to 760 mm. pressure.

4. Hydrogen:

Hydrogen, without further purification, was used from a cylinder produced by the National Cylinder Gas Company.

5. Benzoic Acid:

Merck's reagent grade benzoic acid, guaranteed to contain no more than 0.5 per cent impurities, was used without further purification.

B. Apparatus and Procedure

1. Measurement of Materials:

Catalyst and benzoic acid were weighed on an analytical balance on tared watch glasses. The benzoic acid was transferred to the hydrogenation bottle by means of a metal spatula; with the catalyst it was more feasible to use a camel's-hair brush.

Quinoline samples were measured in an atmosphere of nitrogen by means of the apparatus diagrammed in Figure 3. This apparatus allowed the rapid measurement of a sample with an accuracy of better than two per cent. The glass wool filter was used to remove small particles which otherwise would cause erratic results (58).

Acetic acid was measured in a graduated cylinder. Normally the acetic acid was placed in the hydrogenation bottle and the quinoline was then added directly from the calibrated tube. However, for those runs in which products were isolated, the quinoline was first run into a weighing bottle in order to get more accurate weight. The quinoline was then transferred to the hydrogenation bottle and the weighing bottle washed out with acetic acid.

All glassware used with materials to be hydrogenated was cleaned with cleaning solution, thoroughly rinsed with distilled water, and dried in an oven.

2. Hydrogenation:

Hydrogenations were all carried out in a standard Parr low-pressure hydrogenation apparatus whose total volume, including that of the hydrogenation bottle, was 4.43 liters. The shaker was

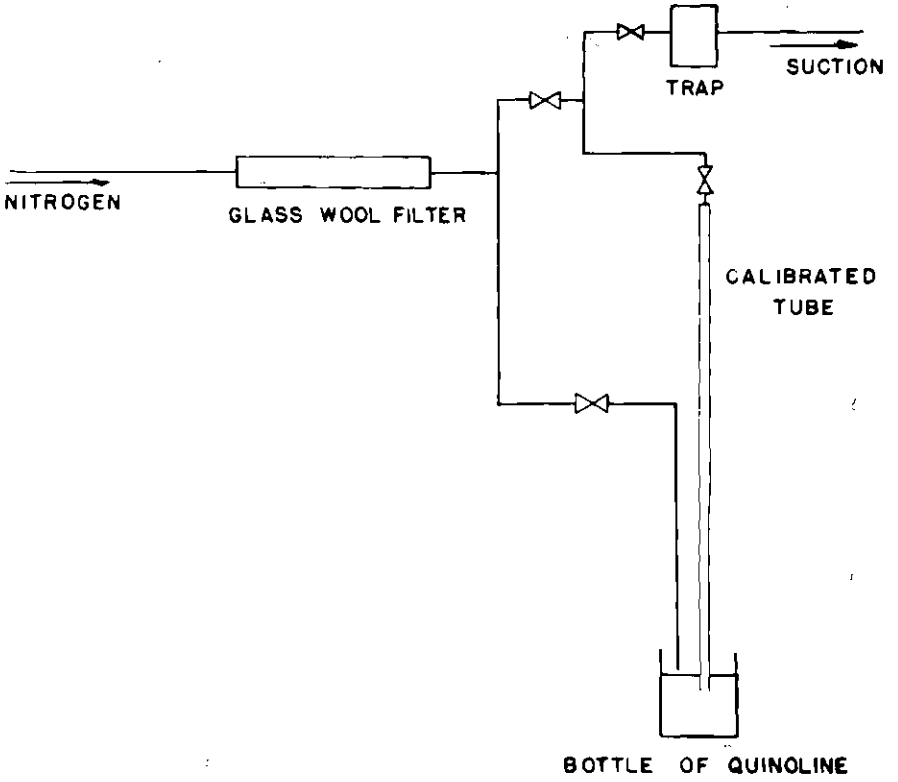


FIGURE 3.
QUINOLINE SAMPLING APPARATUS.

adjusted at about 200 cycles per minute. In place of the metal shield a jacket was used through which water from a constant temperature bath was circulated. The pressure guage on the hydrogenation apparatus was divided into divisions of 0.25 pound per square inch. However, the pressure could easily be estimated to 0.05 pound per square inch. When runs were made at 16 pounds per square inch, or lower pressures a mercury manometer was used.

The hydrogenation bottle, containing the acetic acid and quinoline, was placed in the water jacket. When the temperature within the bottle reached that of the circulating water, the catalyst was added. The bottle was inserted in the apparatus and alternately evacuated and filled with 50 pounds per square inch pressure of hydrogen. This operation was repeated three times. The pressure in the tank was then slowly raised to the desired amount and the shaker was started. From the time the catalyst was added until the beginning of the run usually took about seven minutes.

During the run the hydrogen pressure, water-bath temperature, and temperature of the hydrogen tank and the time were recorded.

Both before and after a run the brass tube leading to the hydrogenation bottle was cleaned with a pipe cleaner immersed in methanol. Before a run it was dried in a stream of hydrogen.

Between runs an empty hydrogenation bottle was connected to the apparatus, and evacuated.

Before being used the rubber stoppers used on the apparatus

were boiled in a 15 per cent solution of sodium hydroxide to remove sulfur. All traces of alkali were then removed by first washing and then boiling in distilled water. As an added precaution, a blank run was made with each new rubber stopper in order to remove anything still remaining which might be soluble in acetic acid.

3. Isolation of Products:

Immediately after hydrogenation the spent catalyst was removed by filtering the hydrogenated mixture through a sintered-glass funnel which had been cleaned with aqua regia. Most of the acetic acid was then distilled off, usually under reduced pressure. The acid solution was transferred to a beaker, cooled, and made basic with concentrated sodium hydroxide. The products were then obtained by extracting with benzene and subsequently removing the benzene by distillation.

IV. DISCUSSION OF RESULTS

A. The Hydrogenation of Quinoline

1. Review of the Literature:

Quinoline has been hydrogenated by a number of investigators using a wide variety of catalysts and conditions (2, 10, 15, 32, 33, 40, 41, 42, 46, 47, 57, 59). It has been found that quinoline readily hydrogenates to 1, 2, 3, 4-tetrahydroquinoline. Only once has the formation of the 5, 6, 7, 8-tetrahydro compound been reported, and then it constituted only one per cent of the product (59).

The formation of decahydroquinoline requires more vigorous conditions. Platinum, however, is a sufficiently active catalyst to give the deca-form even when the hydrogenation is carried out at approximately room temperature and a pressure of only a few atmospheres (32, 40). Two stereoisomers are possible. Many investigators report only the trans form; others have found that both the cis and the trans form result from hydrogenation. One possible explanation of this is that the less stable cis is converted into the trans form, the extent of the conversion depending upon the conditions of hydrogenation. It has been shown that if cis decahydroquinoline is boiled with hydrochloric acid it is converted into the trans form (12).

2. The Variation of the Rate of Hydrogenation with Time:

Graph 1 shows a first order plot for the hydrogenation of

quinoline. This run was made using conditions which were standard in this work: 0.2000 grams of catalyst B; 50 ml. of acetic acid; about 0.02 mole of hydrogen-acceptor; an initial hydrogen pressure of about 64 pounds per square inch absolute and a temperature of 30° for the solution.

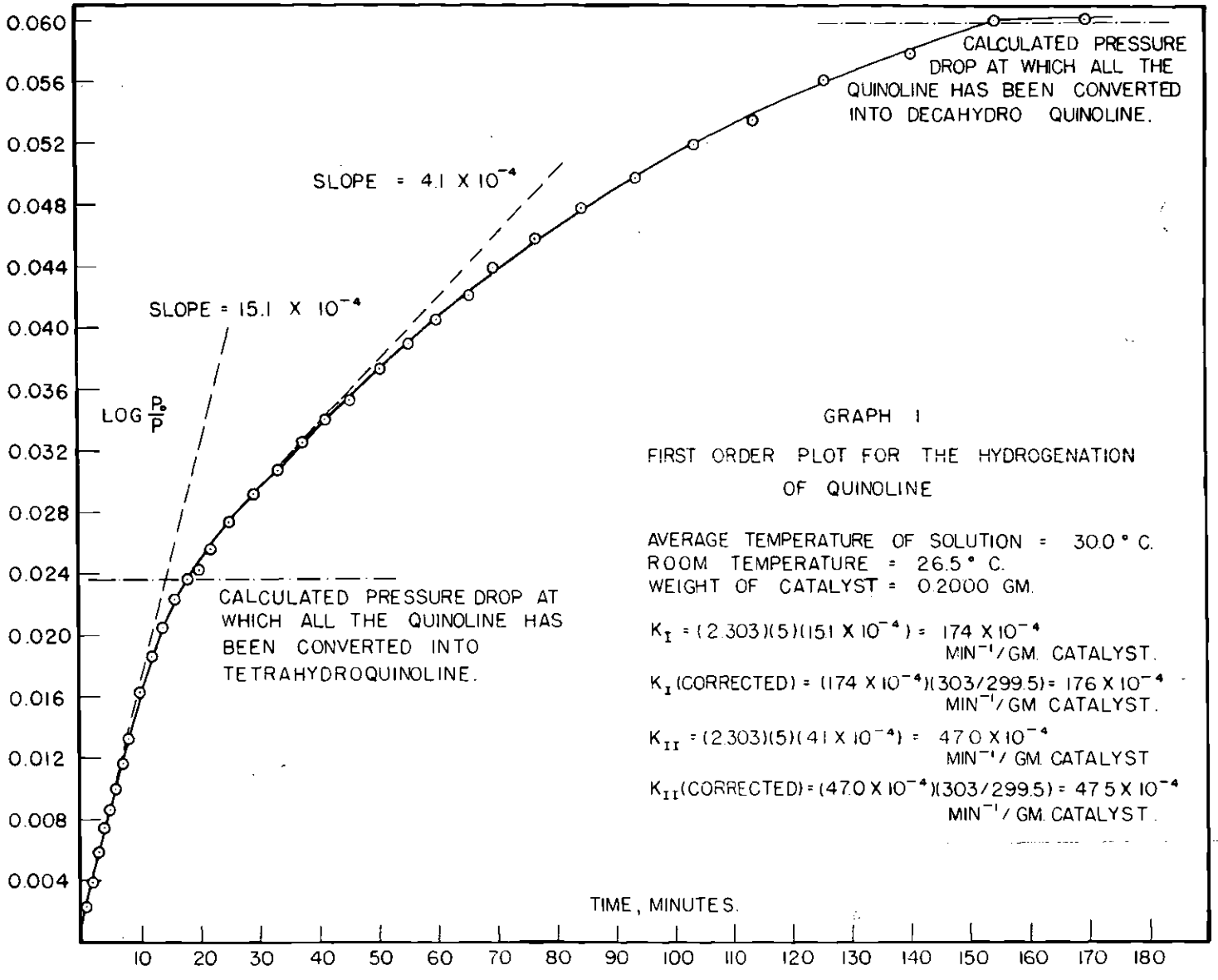
A study of Graph I leads to a number of conclusions.

1. Quinoline hydrogenates quantitatively to decahydroquinoline.

2. During the first minute of the reaction there is a rapid uptake of hydrogen. This results from the rapid reduction of PtO_2 and, as will be shown later, the rapid adsorption of hydrogen on the bare catalyst surface.

3. The rate of hydrogenation of quinoline to tetrahydroquinoline is approximately constant over most of the range, decreasing somewhat after most of the quinoline has been hydrogenated. Careful examination of the curve, however, shows that this decrease in rate takes place over the entire hydrogenation, but is so slight during the initial part of the run that the data appear to define a straight line. The curvature of the first order plot was shown by making runs in which more frequent readings were taken and larger amounts of quinoline were hydrogenated, thereby enlarging the curve.

The decrease in rate with time is readily explained in terms of theory previously developed. As the concentration of hydrogenated product builds up, it is adsorbed on the catalyst surface along with quinoline. Either the hydrogenated pyridine ring or the unsaturated benzenoid nucleus can be adsorbed. The latter will, of course, hydrogenate to give decahydroquinoline. Thus we would expect to



GRAPH 1

FIRST ORDER PLOT FOR THE HYDROGENATION OF QUINOLINE

AVERAGE TEMPERATURE OF SOLUTION = 30.0 ° C.
ROOM TEMPERATURE = 26.5 ° C.
WEIGHT OF CATALYST = 0.2000 GM.

$K_I = (2.303)(5)(15.1 \times 10^{-4}) = 174 \times 10^{-4}$ MIN^{-1}/GM. CATALYST.

K_I (CORRECTED) $= (174 \times 10^{-4})(303/299.5) = 176 \times 10^{-4}$ MIN^{-1}/GM CATALYST.

$K_{II} = (2.303)(5)(4.1 \times 10^{-4}) = 47.0 \times 10^{-4}$ MIN^{-1}/ GM. CATALYST

K_{II}(CORRECTED) $= (47.0 \times 10^{-4})(303/299.5) = 47.5 \times 10^{-4}$ MIN^{-1}/ GM. CATALYST.

find some decahydroquinoline present in a partially hydrogenated mixture and some evidence, although inconclusive, indicates that this is the case. Quinoline (9.7 grams) was allowed to adsorb 98 per cent of the calculated amount of hydrogen required to convert it completely to the tetrahydro derivative.

The hydrogenated product was isolated and distilled through a 15-inch Vigreux column under reduced pressure. Four drops were obtained of a low boiling fraction, but it could not be characterized because it was contaminated. This fraction distilled at a temperature of 82°C and a pressure of 12mm. of mercury. At this pressure we would expect decahydroquinoline (normal boiling point is 205°C) to boil at a temperature about 10° below this. However, 82°C is considerably lower than the temperature at which quinoline (normal boiling point is 238°C) or tetrahydroquinoline (normal boiling point is 251°C) would come over.

4. The rate of hydrogenation of tetrahydroquinoline to decahydroquinoline rapidly decreases. This is because the saturated pyridine ring is competitively adsorbed with the unsaturated benzene ring. The effect of products was small in the first step of the hydrogenation of quinoline because the pyridine ring has a far greater tendency to be adsorbed than the unsaturated benzene or the hydrogenated pyridine ring. However, it appears that the tendency for the latter two nuclei to adsorb is of the same magnitude. Thus we have competitive adsorption, and, by Equation (15), as the concentration of the product builds up the observed rate decreases.

5. The rate constant for this run, corrected for variations in the temperature of the hydrogen gas, is 176 x 10^{-4} reciprocal minutes per gram of catalyst for the hydrogenation of quinoline to tetrahydroquinoline; for the hydrogenation of tetrahydroquinoline to decahydroquinoline it is 47.5 x 10^{-4}. The average values of the rate constants for many runs are 180 x 10^{-4} and 40 x 10^{-4} reciprocal minutes per gram. These rate constants are for the volume of the system studied which is 4.43 liters.

3. Effect of Temperature:

On page 37 is a graph correlating the logarithm of the rate constant with the reciprocal of the absolute temperature for the hydrogenation of quinoline to tetrahydroquinoline. From the slope of the straight line thus obtained, the apparent energy of activation has been calculated to be 6,040 calories per mole. This is in excellent agreement with the value observed by Trimble (58).

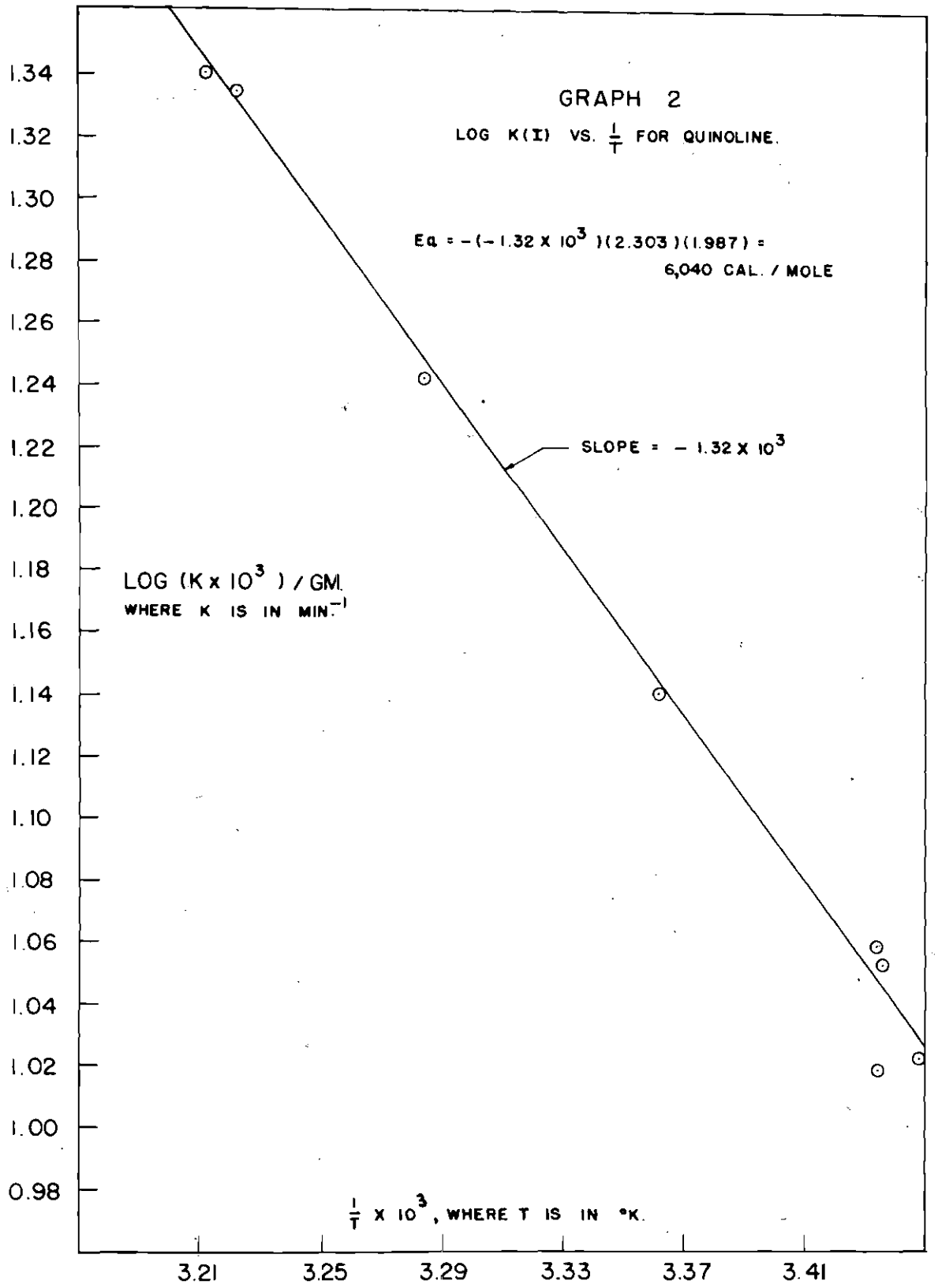
4. Effect of Hydrogen Pressure:

Table (III) shows the variation of the rate constant with hydrogen pressure for the reduction of quinoline to tetrahydroquinoline. These runs were made using catalyst A.

Table (III)

Variation of the Rate Constant with Hydrogen Pressure

Pressure, p.s.i.a.	Rate Constant, $Min^{-1}/Gm.$
64	156
32	158
16	139
7	122


GRAPH 2
LOG K(I) VS. $\frac{1}{T}$ FOR QUINOLINE.
Eq = $-(-1.32 \times 10^3)(2.303)(1.987)$ =
6,040 CAL. / MOLE
SLOPE = -1.32×10^3
LOG $(K \times 10^3)$ / GM.
WHERE K IS IN MIN.$^{-1}$
$\frac{1}{T} \times 10^3$, WHERE T IS IN °K.
1.34
1.32
1.30
1.28
1.26
1.24
1.22
1.20
1.18
1.16
1.14
1.12
1.10
1.08
1.06
1.04
1.02
1.00
0.98
3.21
3.25
3.29
3.33
3.37
3.41

The data indicate the rate constant is independent of pressure. The slight decrease observed at low pressures is probably not significant. One possible explanation is that there was a slight increase in the temperature of the hydrogen cylinder during the course of the run. During later work it was observed on numerous occasions that radiation from the motor heats the surrounding area.

5. Effect of the Concentration of Hydrogen-Acceptor:

Trimble (58) found the rate of hydrogenation of quinoline is zero order with respect to the concentration of hydrogen-acceptor between concentrations of 0.01 mole to 0.06 mole per 50 ml. of acetic acid. The invariance of the rate with respect to hydrogen-acceptor was confirmed between concentrations of 0.02 and 0.04 mole per 50 ml. of acetic acid.

6. Effect of Changing Catalysts:

The effect of catalyst sample upon the rate constant is given in Table IV. For purposes of comparison, rate constants are also given for benzoic acid and 6-methylquinoline.

Table IV

Effect of Catalyst Sample Upon the Rate Constant

Hydrogen-Acceptor	Rate Constant, in $Min.^{-1}/Gm.$ Catalyst A	Catalyst B	Rate B/Rate A
Benzoic Acid	206	216	1.05
Quinoline	156	180	1.15
6-Methylquinoline	94	118	1.25

It can be seen that the correlation is poor. This is especially true when different types of rings are being hydrogenated. Catalyst B is considerably more active than A for a pyridine ring, but has almost the same activity for a benzenoid nucleus. In fact, in the hydrogenation of 6-methyl-1, 2, 3, 4-tetrahydroquinoline, catalyst A is slightly more active. The ratio of Rate B/Rate A is 0.96.

7. The Rate of Adsorption of Hydrogen:

In order to obtain some idea as to the rate of adsorption of hydrogen, 0.3000 grams of catalyst A and 50 ml. of acetic acid were placed in a hydrogenation bottle and the normal hydrogenation procedure was followed. It was found that at 30°C the catalyst adsorbs 0.20 pounds per square inch of hydrogen in a period of 18-20 seconds. No further uptake of hydrogen was observed.

It was pointed out in a previous section (Page 33) that the initial rapid uptake of hydrogen indicates the reduction of the PtO_2 proceeds rapidly. The above experiment, however, indicates that the adsorption of hydrogen also proceeds rapidly, at least in the absence of hydrogen-acceptor.

To demonstrate that the adsorption of hydrogen on the catalyst surface is rapid even in the presence of hydrogen-acceptor, a normal hydrogenation of quinoline was halted by stopping the shaker. During the next few minutes there was no change in hydrogen pressure. When the shaker was started again, however, there was a rapid uptake of hydrogen. This offers strong evidence that the adsorption step is rapid. When the shaker is stopped, hydrogen and quinoline can no

longer be adsorbed since diffusion of the gas is very slow. The reaction, however, continues between quinoline and hydrogen that has already been adsorbed. As a result, part of the catalyst surface becomes bare and, when shaking commences, there is a rapid uptake of hydrogen.

B. The Effect of Methyl-substitution on Hydrogenation

1. Review of the Literature:

von Braun and co-workers studied the hydrogenation of all of the methyl-substituted quinolines except 5-methylquinoline (9, 10). Using a nickel catalyst under mild conditions they found that substitution in the benzene ring prevented preferential hydrogenation of that ring. Only 1, 2, 3, 4-tetrahydro derivatives were obtained. However, when a methyl group was substituted on the pyridine nucleus, both the 1, 2, 3, 4- and the 5, 6, 7, 8-tetrahydro derivatives were obtained. With 2-methylquinoline the 5, 6, 7, 8-tetrahydro derivative constituted 4 per cent of the product; with 3-methylquinoline and 4-methylquinoline, the 5, 6, 7, 8-tetrahydro derivative constituted 33 per cent of the product.

6-methyldecahydroquinoline has been prepared using a platinum catalyst (24). If high temperatures and pressures are employed, a nickel catalyst will reduce a methylquinoline to the deca form (46).

2. Dependence of the Rate on Concentration, Pressure and Amount of Catalyst:

Normally runs were made using 0.2000 grams of catalyst, 50 ml.

of acetic acid, 0.02 moles of hydrogen-acceptor and 64 pounds per square inch absolute pressure. However, a number of runs were made with the methylquinolines studied to determine the dependence of the rate upon the concentration of hydrogen-acceptor, the amount of catalyst, and the hydrogen pressure.

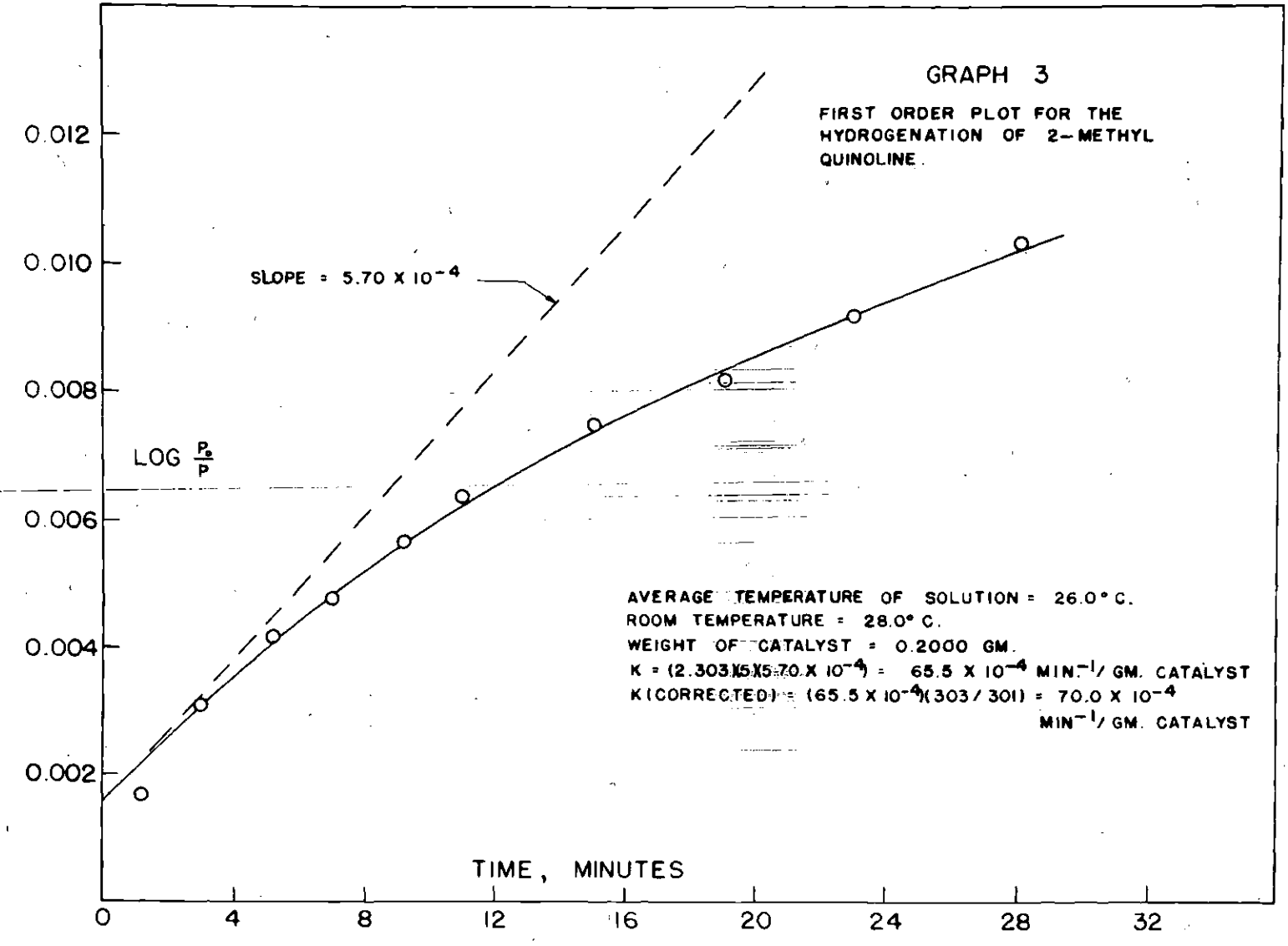
As observed with quinoline, the rate is independent of the concentration of hydrogen-acceptor between concentrations of 0.02 and 0.04 mole per 50 ml. of acetic acid. The rate is directly proportional to the amount of the catalyst. Between pressures of 16 and 64 pounds per square inch absolute the rate is independent of hydrogen pressure.

3. The Variation of the Rate of Hydrogenation with Time:

The first order plots for the hydrogenation of the methylquinolines substituted in the benzene ring are similar to the curve for quinoline.

The hydrogenation of 2-methylquinoline and 4-methylquinoline was somewhat different. The rate of reaction decreased rapidly as the hydrogenation proceeded. This is shown by Graph 3 which is a first order plot for the hydrogenation of 2-methylquinoline.

A number of runs were made in which the hydrogenation was stopped, the spent catalyst was removed, and fresh catalyst was added. If this was done toward the beginning of the run, hydrogenation proceeded as before, and a rapid decrease in the rate was observed. However, if the fresh catalyst was added after a little more than two moles of hydrogen per mole of quinoline had been


GRAPH 3
FIRST ORDER PLOT FOR THE HYDROGENATION OF 2-METHYL QUINOLINE.
SLOPE = 5.70 X 10⁻⁴
LOG P₀/P
0.012
0.010
0.008
0.006
0.004
0.002
TIME, MINUTES
0
4
8
12
16
20
24
28
32
AVERAGE TEMPERATURE OF SOLUTION = 26.0° C.
ROOM TEMPERATURE = 28.0° C.
WEIGHT OF CATALYST = 0.2000 GM.
K = (2.303)(5)(5.70 X 10⁻⁴) = 65.5 X 10⁻⁴ MIN.⁻¹/ GM. CATALYST
K(CORRECTED) = (65.5 X 10⁻⁴)(303/301) = 70.0 X 10⁻⁴ MIN⁻¹/ GM. CATALYST

adsorbed, then no poisoning effect was observed.

These observations might indicate that 2-methyl and 4-methylquinoline act as catalyst poisons. More likely, the desorption of one of the tetrahydro derivatives is slow.

It is interesting to note that if fresh catalyst is added after a little more than two moles of hydrogen per mole of quinoline has been adsorbed, the rate of hydrogenation of 2-methylquinoline is almost as rapid as the initial rate; with 4-methylquinoline, the rate of hydrogenation is twice as rapid as at the beginning of the run.

4. The Effect of Substitution on the Rate:

Table V gives the effect on the rate constant of methyl substitution on the benzene ring. Table VI gives the rate constants for methyl-substitution on the pyridine nucleus. The latter rate constants were computed by extrapolating the curves and obtaining the slope at time equal to zero.

All rate constants are for the hydrogenation of 0.02 moles of hydrogen-acceptor in a solution of 50 ml. of acetic acid using catalyst B. The temperature of the solution and the hydrogen in the tank is 30°C. The total volume, including the hydrogenation bottle, is 4.43 liters.

No attempt will be made to correlate the observed reactivities with the structure. Probably a number of factors are involved. These would include steric effects and the electronic density throughout the ring. The possibility that a substituted group is adsorbed to a certain extent on the catalyst surface is still another possibility.

The high rate constant observed for 8-methylquinoline seems especially significant. This represents the first reported case where the addition of a methyl group to an unsubstituted aromatic ring increases the rate of hydrogenation.

It should be noted that the rates of hydrogenation for the 5-methyl, the 6-methyl and the 7-methylquinoline are all about the same. This is in contrast to what has been observed with pyridine (56).

Substitution in the pyridine ring seems to greatly diminish the rate.

Table V

Effect of Methyl Substitution on the Rate Constant

Quinoline	Rate Constant x 10^4 Min.$^{-1}$/Gram	Relative Rates	Estimated Accuracy, Per Cent
Quinoline	180	1.00	2
5-Methylquinoline	109	0.61	10
6-Methylquinoline	118	0.60	3
7-Methylquinoline	108	0.60	3
8-Methylquinoline	342	1.90	3

Table VI

Effect of Methyl Substituents on the Rate Constant

Quinoline	Rate Constant x 10^4 Min.$^{-1}$/Gram	Relative Rates	Estimated Accuracy, Per Cent
Quinoline	180	1.00	2
2-Methylquinoline	83	0.46	10
4-Methylquinoline	7	0.04	50

Table VII gives the effect of methyl substitution on the rate constants for the hydrogenation of the 1, 2, 3, 4-tetrahydroquinoline to the deca. Because the hydrogenation proceeded so slowly, these rates are not very accurate. The possibility of catalyst poisoning must also be considered.

Table VII

Effect of Methyl Substitution on the Rate Constant for the Hydrogenation of Tetrahydroquinolines

Quinoline	Rate Constant x 10^4 Min.$^{-1}$/Gram	Relative Rates	Estimated Accuracy, Per Cent
Quinoline	46	1.00	15
5-Methylquinoline	22	0.48	100
6-Methylquinoline	23	0.50	30
7-Methylquinoline	13	0.28	50
8-Methylquinoline	10	0.22	50

5. The Effect of Substitution on the Energy of Activation:

Table VIII gives the effect of substitution on the energy of activation for the hydrogenation of a methylquinoline, substituted in the benzene ring, to the corresponding 1, 2, 3, 4-tetrahydro derivative. There is no significant change with structure. Thus the energy of activation for the hydrogenation of the pyridine ring appears to be about 5800 calories per mole.

Table VIII

Effect of Substitution on the Energy of Activation

Quinoline	Apparent Energy of Activation, Cal./Mol.	Estimated Accuracy, Per Cent
Quinoline	6,000	5
6-Methylquinoline	6,000	10
7-Methylquinoline	5,800	10
8-Methylquinoline	5,400	10

Kinetic data for the second step of the reduction was also taken at different temperatures. Since these rate constants can not be accurately obtained, it was very difficult to determine the energy of activation. It appears, however, that the energy of activation for the reduction of the benzene ring is about 10,000 calories per mole.

The energy of activation for the hydrogenation of 2-methylquinoline was found to be about 6,600 calories per mole. Since it was difficult to obtain good rate constants due to the rapid

V. SUGGESTIONS FOR FURTHER STUDY

A. Completion of the Work with the Quinoline Nucleus

The hydrogenation of 3-methylquinoline should be investigated in order to have a complete study of the methylquinolines. 3-methylquinoline can be conveniently prepared from o-nitrobenzaldehyde and propionaldehyde by the method of Willmott and Simpson (62).

Studies of the polymethylquinolines and quinoline carboxylic acids would probably be quite fruitful. Ease of synthesis should be an important criterion in determining what compounds to study.

If a study of the rate of hydrogenation of a known mixture of tetrahydroquinoline and decahydroquinoline were made, it would be possible to verify the conclusions reached in the discussion of results concerning the effect of product on the rate of hydrogenation.

A study of the products resulting from the hydrogenation of the methylquinolines would be of considerable interest. This would be especially true in the case of quinolines substituted in the pyridine ring. Probably the ratio of hydrogenation in the benzenoid ring to that in the pyridine ring would not be the same as observed by von Braun (9, 10) because of the great differences in the conditions of hydrogenation.

Considerable effort was expanded during this investigation to find an effective method for analyzing the products of hydrogenation, but little success was achieved. It is a complicated problem since the mixture to be analyzed may contain four possible compounds: the original quinoline, the decahydroquinoline, the 1, 2, 3, 4-tetra-

decrease in the rate, the estimated accuracy of this energy of activation is probably only 15 per cent.

hydroquinoline and the 5, 6, 7, 8-tetrahydroquinoline. To make matters worse, it must be remembered that small quantities are to be analyzed.

Probably the most promising method is the separation of the 1,2, 3,4-tetrahydroquinoline and the decahydroquinoline from the other two by treatment with benzoyl chloride (9, 10). Since the decahydroquinolines boil about 50°C. below the corresponding 1, 2-3, 4-tetrahydroquinolines, these two could be separated by distillation. On the other hand, the 5, 6, 7, 8-tetrahydroquinolines boil at about the same temperatures as the corresponding quinolines. However, it must be remembered that since the weight of quinoline hydrogenated and the amount of hydrogen adsorbed are known, it is not necessary to have a complete analysis.

Another possible method of analysis would be by potentiometric titrations of each fraction obtained from benzylation. If an aliquot was used for the titrations, this method could be combined with distillation and would give a good measure of the total basicity.

If analysis is to be effected by distillation, it would be desirable to obtain a suitable distillation base. Benzyl ether was tried, but was unsatisfactory due to its lack of stability. Perhaps o-diphenylbenzene would be suitable.

B. Basic Studies on the Effect of Substituted Groups:

It would be interesting to see if any correlation could be

established between the electronic influence of a substituted group and its effect upon the rate of hydrogenation of an aromatic nucleus. The effect of substitution on the energy of activation could also be studied.

Unfortunately, this problem would be rather difficult to carry out since, in order for the results to have any meaning, compounds which hydrogenate virtually quantitatively to a single product would be required. Thus it would be necessary to investigate many compounds which may prove to be unsatisfactory. Moreover, the correlation sought might not be found even if sufficient data could be obtained. While there seems to be little doubt that the electronic influence of a substituted group is important in determining the rate, other factors, as previously mentioned, are also important and might prevent a correlation.

C. Basic Studies on Competitive Hydrogenations:

On page 18 there is derived an equation which relates the important variables in a competitive hydrogenation. As emphasized in the theoretical discussion, the derivation of this equation is based on a concept of hydrogenation which may be wrong. However, if it were possible to prove the approximate validitly of this equation, it would not only be valuable in itself, but would also substantiate the concept of the mechanism of hydrogenation on which the derivation is based. Competitive hydrogenation studies also might furnish information as to where the molecule is adsorbed.

Competitive hydrogenations could easily be studied with a simple system such as benzoic acid and toluene. These compounds

are ideal since they can be readily obtained in high purity. Moreover, the four component mixture resulting from incomplete hydrogenation can be analyzed easily. Thus it would be relatively simple to study the rate of hydrogenation and the composition of the products for various molar fractions of toluene to benzoic acid.

The work on competitive hydrogenations could also be made to include the effect of a substituted group on the adsorption coefficient.

D. Effect of Piperidine on the Hydrogenation of Benzene:

It has been postulated in this thesis that a hydrogenated pyridine nucleus is competitively adsorbed in the presence of a benzenoid nucleus. This could be proved by hydrogenating benzene in the presence of piperidine. A marked decrease should occur in the rate. The magnitude of this decrease will depend upon the molar ratio of piperidine to benzene.

E. The Use of Glyoxal in the Synthesis of the Homologs of Quinoline:

Kulisch (37) reported that the condensation of ortho-toluidine with glyoxal gave 35 to 40 per cent yields of quinoline. While this method is of no value in the synthesis of quinoline itself, it could be an extremely useful preparative method for some of the homologs of quinoline which are difficult to prepare.

In this work it was attempted to prepare 5-methylquinoline by the condensation of glyoxal with 2, 3-dimethylaniline, prepared

in 94 per cent yield by the reduction of 3-nitro, 1-2-dimethylbenzene with iron and hydrochloric acid (34). After four attempts, none of which gave any product, this phase of the project was abandoned.

Because of the potential usefulness of this method of synthesis, this reaction seems worthy of further investigation. Some of the reasons why difficulties have been experienced might include:

1. The glyoxal, which is extremely reactive, may not have been present as the monomeric form. The syntheses attempted used a 30 per cent glyoxal solution (Eastman's technical grade), the bisulfite addition product of glyoxal, and glyoxal produced during the hydrolysis of 2, 3-dichlorodioxane in boiling water.

2. No attempt was made to isolate the intermediate. Any future work certainly should do this, since this would show whether the difficulty lies in condensation or ring closure.

3. The electron donating methyl group in the 1-position may decrease the acidity of the hydrogens on the methyl group in the 2-position to such an extent that ring closure is no longer possible. In this case the synthesis is of no value unless there are electron attracting groups on the ring. It should also be pointed out that steric factors may be involved.

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